

Production of Compounds labelled with Carbon-14 from Carbon-14 Dioxide accelerated in an Electric Field

It is well known that hot radioactive carbon-14 and tritium atoms can be used to produce labelled organic compounds often with very high specific activity¹. This convenient method requires nevertheless a high neutron flux, often yields a cumbersome mixture of labelled compounds and moreover radiation damage frequently produces undesired effects. For these reasons, I have devised a new method in order to avoid such difficulties.

The procedure developed to prepare labelled compounds is based on the acceleration of carbon-14 dioxide by submitting it to a voltage of 500 V. Under such conditions, carbon-14 is able to react with organic compounds or radicals. In the apparatus illustrated in Fig. 1, the two steel electrodes are removable. A thin layer of the organic material to be treated (about 2–10 mgm.) is spread on the cathode. The two bulbs of the cell have ground-glass joints. The cell is connected to a vacuum line and evacuated for an hour to a pressure of 10^{-6} mm. mercury. After carbon-14 dioxide has been admitted at a pressure of 0.5×10^{-1} mm. mercury, an applied voltage of 500 V. produces a discharge of 100–150 μ amp. The cell is then removed and the organic layer diluted in a suitable solvent. After carrier is added, the active sample is purified chemically until it has constant activity. Indeed, part of the activity of the sample is to be attributed to adsorbed carbon-14 dioxide and is consequently labile. After this radiochemical separation, measurements of the radioactivities isolated are carried out by means of a gas-flow counter. By this method, the following simple organic molecules of the aliphatic and aromatic series have been labelled: acetamide, citric acid, succinic acid, benzoic acid and benzoates.

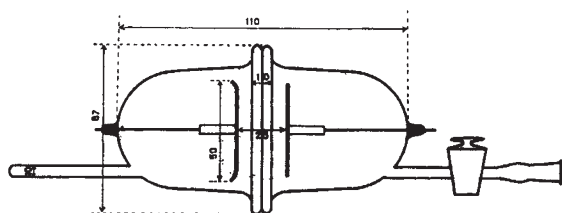


Fig. 1. Diagram of apparatus. Dimensions are in millimetres

In most cases, specific activities are equal to about 0.2 mc./gm. This procedure considerably reduces interference by other adjacent labelled compounds. The specific activities obtained are variable, depending on time of exposure, and increase with the latter. They are also a function of several other factors which are being examined in experiments now in progress. At the same time, the labelling mechanism will be studied. It is hoped that this new labelling technique will be applicable to other radionuclides.

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¹ Rowland, F. S., Turton, C. N., and Wolfgang, R., *Science*, **121**, 715 (1956). Rowland, F. S., and Wolfgang, R., *Nucleonics*, **14**, 55 (1956).

Hydrogen Overpotential on Germanium Electrodes

ELECTRON transfer reactions at the semiconductor–electrolyte interface are of particular interest because it is not known experimentally whether the reaction kinetics depend upon the bulk electron concentration in the semiconductor. Results of recent measurements of the hydrogen evolution reaction on single crystal germanium electrodes are presented here. The electrode potential (versus the normal hydrogen electrode) was measured under suitable conditions of purity for analysis of the mechanism (Table 1).

Table 1. HYDROGEN OVERPOTENTIAL DATA AT GERMANIUM ELECTRODES (23° C. AND 1 M HYDROCHLORIC ACID)

Crystal surface exposed	Bulk electron concentration (cm. ⁻³)	Exchange current (amp. cm. ⁻²)	-b (mV.)*	-Δφ _{i=0} (mV.)†
Unknown	4×10^{14}	1.4×10^{-8}	113	45
Unknown	3×10^{14}	4.7×10^{-8}	102	1.5
(100)	$\sim 10^{14}$	$(2.2 \pm 0.3) \times 10^{-8}$	115 ± 12	29 ± 10
(100)	$\sim 10^{14}$	$(2.3 \pm 0.3) \times 10^{-8}$	109 ± 5	26 ± 6.6
(110)	$\sim 10^{14}$	$(1.0 \pm 0.2) \times 10^{-8}$	116 ± 2	35 ± 4
(111)	$\sim 10^{14}$	$(1.9 \pm 0.4) \times 10^{-8}$	148 ± 9	41 ± 20

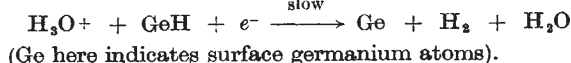
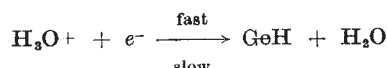
* $b = 2.303 (\delta\eta/\delta \ln i)$ per decade of current.

† Δφ_{i=0} is the rest potential of the electrode.

The case where care was taken to ensure that the crystallographic planes were the same on both *n*- and *p*-type germanium (third and fourth entries in Table 1) shows that variation in the bulk semiconductor electron concentration does not produce a corresponding variation in parameters of the hydrogen evolution reaction.

The fact that Δφ_{i=0} is substantially above zero for most cases shown in Table 1 is interpreted as being due to the dissolution of germanium, that is, the germanium electrode is behaving as a polyelectrode¹. Such polyelectrode behaviour makes it impossible to obtain the stoichiometric number, ν , for the hydrogen evolution reaction from an analysis of the overpotential–current curve as η goes to zero². However, for one electrode Δφ_{i=0} is essentially zero and here an analysis of the η versus i curve gives $\nu = 1.06$.

Bockris (personal communication) has recently shown that a germanium electrode (supposedly the (110) crystal plane) is covered with a monolayer of adsorbed hydrogen atoms. When this fact is combined with the fact that the Tafel slope is $-2RT/F$ and the stoichiometric number is 1, it can be shown that the only possible simple mechanism for the hydrogen discharge reaction from acid solution is³:



This presupposes the mechanism of the hydrogen evolution reaction to be the same on all the germanium crystal surfaces and that the germanium electrode is behaving like a metallic electrode. A more detailed discussion of this work will appear elsewhere.

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¹ Frumkin, *Z. phys. Chem.*, **160**, 116 (1932). Wagner and Traud, *Z. Electrochem.*, **44**, 391 (1938). Bockris, "Modern Aspects of Electrochemistry", 253 (Butterworths Sci. Pub., 1954).

² Bockris and Potter, *J. Electrochem. Soc.*, **99**, 169 (1952).